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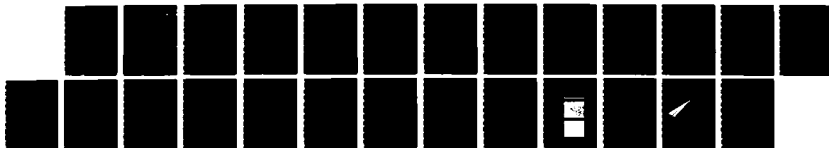
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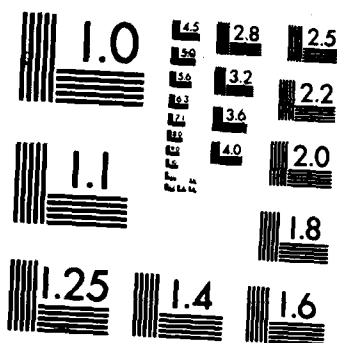
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CHEMICAL REACTIONS AT THE Au/InP INTERFACE

by

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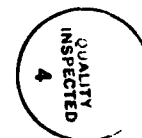
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# CHEMICAL REACTIONS AT THE Au/InP INTERFACE

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## Abstract

Chemical reactions at the Au/InP interface were investigated in the temperature range 25°–510°C by x-ray diffractometry, scanning electron microscopy and energy dispersive X-ray analysis. The samples were prepared by depositing gold films onto clean InP (100) single-crystal substrates under  $10^{-9}$  torr vacuum. Spots appeared in SEM micrographs of the deposited film of a sample annealed at room temperature for 35 days, indicating that a solid state reaction had occurred. After the sample was heated to 330°C under flowing N<sub>2</sub> gas,  $\zeta_1$  dendritic islands were observed in the film. A 365°C anneal turned the color of the Au film from yellow to pink, and Au,  $\zeta_1$  and Au<sub>2</sub>P<sub>3</sub> were identified by X-ray diffractometry. In reacting with the InP substrate,  $\zeta_1$  produced silver-colored  $\gamma$  and more Au<sub>2</sub>P<sub>3</sub> at 450°C. With respect to InP,  $\gamma$  was relatively stable, and further reactions were minimal even when the sample was annealed at 510°C for 40 min under atmospheric-pressure N<sub>2</sub>. The ternary phase diagram for the bulk Au–In–P system provides the basis for understanding the sequence of the above results and much of the information in the literature about Au/InP interfacial reactions.

## I. Introduction

Indium phosphide is an important III-V compound semiconductor that is currently used in several optoelectronic and high speed devices. Gold is the most commonly used contact metal for InP substrates. As deposited, gold contacts form a good Schottky barrier. However, after the annealing required for device processing, the barrier usually decreases and the contact may turn Ohmic. During the last decade, various techniques have been used to study reactions at the Au/InP interface, and several interesting observations have been reported.<sup>1-17</sup> However, few of the investigators discussed the metal/compound-semiconductor reaction from the chemical point of view, perhaps because the bulk solid-state reactions between Au and the III-V compound semiconductors had not been thoroughly investigated.

Kim, et al.<sup>1</sup> used Secondary Ion Mass Spectrometry (SIMS) to study the degradation of the Au/InP Schottky barrier after the sample underwent heating cycles. They observed the interdiffusion of Au and In at temperatures above 350°C, and a catastrophic degradation of the Schottky barrier at 500°C. Tuck, et al.,<sup>4</sup> also using SIMS, have found the out-diffusion of In at a temperature as low as 340°C and observed that the character of the barrier contact changes from Schottky to Ohmic at 400°C. Szydlo, et al.,<sup>5</sup> using Auger combined with Ar<sup>+</sup> sputtering, observed the degradation of the Schottky barrier and the interdiffusion of Au, In, and O at annealing temperatures above 340°C. Keramidas, et al.,<sup>9</sup> after annealing samples at 420°C for 7 minutes, observed the formation of the intermetallic compound Au<sub>9</sub>In<sub>4</sub> and lateral spreading of the Au-based contact. Piotrowsky, et al.,<sup>10</sup> using He<sup>+</sup> Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffrac-

tion (XRD), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM), observed the formation of an Au(In) solid solution,  $\text{Au}_3\text{In}$ , and  $\text{Au}_2\text{P}_3$  at temperatures in the range 320–360°C, and saw the film change in color from golden to pink. Barnes and Williams,<sup>11</sup> using SEM, XRD, Auger Electron Spectroscopy (AES), and RBS, studied the Au-5%Sn/InP Ohmic contact. They found  $\text{Au}_4\text{In}$ , AuSn and polycrystalline InP for annealing temperatures above 320°C and  $\text{Au}_3\text{In}_2$  above 410°C; the contact was non-Ohmic below 350°C, and the contact resistance increased drastically above 420°C. Thus, only a narrow range of annealing temperatures produced a low-resistance contact. Camlibel, et al.,<sup>13</sup> using interference microscopy, cathode-luminescence, SEM, and Energy-Dispersive X-Ray (EDX) microanalysis, found compounds of Au with both In (Au:In::85:15) and P (Au:P::34:66) in films of samples annealed to 420°C. Brasen et al.<sup>15</sup> used TEM to study laser-induced deposits of Au on (001) InP, and found  $\text{Au}_4\text{In}$ .

The above studies were all performed on samples that were annealed under an atmospheric pressure of  $\text{N}_2$ ,  $\text{H}_2$ , or other inert gases. Several other studies have been conducted in vacuo, either with or without annealing. Williams, et al.<sup>2</sup> used AES, Low-Energy Electron Diffraction (LEED), SEM, EDX, and electrical measurements to investigate Au/InP chemistry. They observed that the Schottky barriers were reduced for annealing *in vacuo* above 300°C, the contact became Ohmic at 400°C, and diffusion of Au into the InP substrate occurred at all temperatures above 400°C. Hiraki, et al.<sup>3</sup> have studied the depth profile of the Au/InP interface region by  $\text{Ar}^+$  ion sputtering and AES, and claimed that Au and the semiconductor reacted readily, even at room temperature. Chye, et al.,<sup>6</sup> using various forms of photoemission spectroscopy and ion-depth profiling techniques, found that extremely thin Au films

interacted strongly with InP, even when deposited on room-temperature substrates. They identified two chemically different forms of P in their spectra. Farrow, et al.<sup>7,8</sup> deposited Au films on substrates held at or below 40°C, and found no evidence for interfacial alloying or interdiffusion by using LEED, RBS, and TEM. Brillson, et al.,<sup>12</sup> using Soft X-Ray Photoelectron Spectroscopy (SXPS), studied this contact and found substantial outdiffusion of both P and In as Au was deposited. Vandenberg et al.,<sup>14</sup> using XRD and *in-vacuo* annealing, observed the formation of a solid solution of In in Au ( $\alpha$  phase) at temperatures above 320°C, the intermetallic compound Au<sub>4</sub>In above 330-340°C, Au<sub>9</sub>In<sub>4</sub> above 390°C, and AuIn<sub>2</sub> above 450°C. Mojzes, et al.<sup>16</sup> used mass spectrometry to study the evolution of volatile P species from Au/InP interfaces, and reported that a reaction occurred that released a large amount of P into the vacuum at 440°C. However, codeposition of Ga with the Au film greatly suppressed the sublimation of P.

The phenomena reported in the literature, related to the reactions of Au thin films on InP single-crystal substrates, are (1) color change of the film,<sup>4,10</sup> (2) diffusion of In into Au and Au into InP,<sup>1,3,5,10-14</sup> (3) diffusion of P into Au,<sup>3,12,13</sup> (4) formation of Au<sub>2</sub>P<sub>3</sub>,<sup>10,13</sup> (5) formation of various Au-In intermetallic compounds,<sup>1,10,11,13,14,15,17</sup> (6) a reduction or disappearance of the Schottky barrier,<sup>1,2,4,5,7,8,11,13</sup> and (7) the evolution of gas-phase P species (i.e., P<sub>2</sub> and P<sub>4</sub>).<sup>16</sup> The temperatures at which specific reactions were reported to occur vary among investigators; this may be caused by the different methods of measuring temperature, different sample preparation, and different ambients and pressures. In general, the lower



the ambient pressure during annealing, the lower the temperatures at which reactions occur.

A great deal of confusion exists in the literature about the nature of the phases in reacted gold films on compound semiconductors. Several investigators discuss the fact that there are solid solutions of Au and In, or that alloys have formed. In fact, there are nine thermodynamically stable phases containing Au and In, (summarized in Table I) as determined by Hiscocks and Hume-Rothery,<sup>18</sup> and all but one of them, the  $\alpha$  phase, are distinct intermetallic compounds. The enthalpy of formation of these compounds per mole of Au is substantial (on the order of 10 kcal/mole).<sup>19</sup> One compound, named  $\psi$ , is stable only above 224°C. Six of the compounds,  $\alpha_1$ ,  $\xi$ ,  $\xi_1$ ,  $\epsilon$ ,  $\gamma$  and  $\psi$ , exist with an appreciable homogeneity range and are thus given Greek-letter designations. This may also have been the cause of some confusion, since different authors refer to the same phase by different chemical formulas. For example,  $\text{Au}_7\text{In}_3$ ,  $\text{Au}_9\text{In}_4$ , and  $\text{Au}_2\text{In}$  are all actually the compound  $\gamma$ . The three most Au-rich phases are gold-colored, whereas both  $\xi_1$  and  $\epsilon$  phases are pink, with  $\epsilon$  being a lighter shade. The remaining three Au-In compounds are silver-colored. For the Au-P and In-P binary systems,  $\text{Au}_2\text{P}_3$  and  $\text{InP}$ , respectively, are the only stable compounds that exist.

The Au-Ga-As ternary phase diagram has been used as a basis for understanding the Au/GaAs system, and much of the interfacial chemistry observed for this system has been explained in terms of bulk thermodynamics.<sup>20,21</sup> The solidus portion of the Au-In-P ternary phase diagram has been mapped recently,<sup>22</sup> and is used as a framework for understanding the chemistry at the Au/InP interface in this study. This paper utilizes the ternary phase diagram to explain many of the liter-

ature results reported above for the interfacial reaction of Au contacts on InP as well as the experimental results of this work. The next section presents the experimental procedure used in this study. Section III presents the results of the experiments, and a discussion follows in section IV. The conclusions of this paper are presented in section V.

## II. Experimental Procedure

The InP single-crystal substrates used in this experiment were (100)-oriented wafers. They were chemically etched with a 2% mixture of bromine in methanol prior to being mounted in an Ultra-High Vacuum (UHV) analysis chamber. Before deposition of Au, the samples were cleaned further *in vacuo* with several cycles that consisted of alternating argon ion bombardment at 1 kev with annealing to 300°C for 10 minutes. After the cleaning cycles, Auger spectra showed a reasonably clean surface with only trace C and O peaks (less than 5% total surface coverage). The gold beams were produced by thermal evaporation from a tungsten basket; an Inficon (model XTM) quartz crystal micro-balance was used to measure and control the evaporation rate. The base pressure was  $10^{-10}$  torr during the *in-situ* measurements and  $10^{-9}$  torr during Au deposition. For a 550Å Au film grown on an InP (100) substrate, the AES spectrum showed an essentially complete coverage of the surface. The wafer then was removed from the vacuum chamber and cleaved into several pieces, which were stored in air for further treatment and analysis. Two samples were annealed in an oven under flowing N<sub>2</sub> gas at atmospheric pressure to various temperatures for 10 minutes to 2 hours. The heating cycles were halted when a visible change in the film occurred, in order to perform experiments to characterize the reaction products.

After being annealed, the samples were analyzed by XRD, SEM, and EDX. The XRD was performed with a standard Phillips X-ray powder diffractometer, which was interfaced to a microcomputer that controlled the scan rate and collected the data digitally. The wafers were simply mounted on the diffractometer, and a powder pattern of the film on the substrate was obtained. The diffraction data were collected at two-theta intervals of  $0.10^\circ$ , with a counting time of 10 sec at each angle; the total time required for a complete scan ( $2\theta$  from 10 to 100 degrees) was three hours in order to obtain a signal-to-noise ratio of better than 50 for the strongest diffraction peaks. The powder patterns thus obtained were compared to those collected as standards for each of the possible intermetallic compounds, as discussed in Ref.21. Several different instruments available in the Materials Science and Biology Departments at UCLA were used to perform the SEM and EDX analyses.

### III. Results

The XRD pattern of the as-deposited Au films showed weak InP peaks from the substrate, Au (222), and strong Au (111) peaks. This result showed that the Au film was highly oriented (oligo-crystalline), with the (111) Au plane parallel to InP (100), and a large enough mosaic spread to ensure that the  $\langle 111 \rangle$  reflections were easily observable. The intensity of the diffraction peaks of the InP substrate was a strong function of the orientation of the single crystal on the diffractometer.

The results of the Au/InP annealing experiments performed for this investigation are summarized in Table II. After being annealed at room temperature for 35 days, the SEM pictures showed that spots had formed in the Au film (Fig.1a). However, the x-ray diffraction pattern did not change noticeably. For a film (sample A) annealed 90 minutes at  $295^\circ\text{C}$

under flowing  $N_2$ , there was still no change observed in either the film color or the XRD pattern. After further annealing at  $330^\circ C$  for 85 minutes, the color of the film was lighter but still yellow. A shoulder appeared on the smaller two-theta side of the Au (111) peak (Fig.2a). This broadening indicated that sufficient In had diffused into the Au film to form a detectable amount of the  $\alpha$  solid solution, with a small enough lattice constant to be observed in the presence of pure Au in the XRD pattern. A small peak at  $2\theta=40.5$  was identified, by comparison with standards, to be the strongest feature of the  $\zeta_1$  intermetallic compound. The SEM picture of this sample showed that the deposited film still fully covered the InP substrate, but a dendritic pattern had formed in the film. After being heated for 60 min at  $365^\circ C$ , the film turned pink in color, the  $\zeta_1$  peak intensified in the XRD pattern, and a very weak  $Au_2P_3$  peak appeared (Fig.2b). The Au peaks had decreased in intensity, but were still present. The SEM picture showed a dendritic pattern similar to that present at  $330^\circ C$  (Fig.1b), and the EDX spectrum revealed that the dendritic islands had a stoichiometry close to  $Au_7In_2$ . For the sample annealed at  $395^\circ C$  for 60 minutes, the color of the film and the SEM micrograph were similar to those of the film annealed at  $365^\circ C$ , but the dendritic islands were denser, the Au (111) peak in the XRD pattern was less intense, and the  $Au_2P_3$  peak was more intense. Sample B was annealed at  $410^\circ C$  for 60 min; the color of the resulting film was pink and the x-ray diffraction pattern showed that the  $\zeta_1$  peaks were much more intense than those of Au. For the sample annealed to  $450^\circ C$  for 25 min., the color turned silvery, all the peaks corresponding to Au and  $\zeta_1$  disappeared from the XRD pattern, and XRD peaks corresponding to  $\gamma$  appeared. Sample B was further annealed to  $450^\circ C$  for 85 minutes, and the silver color turned

faint. The x-ray diffraction pattern showed that the intensities of peaks corresponding to  $\text{Au}_2\text{P}_3$  had increased, with the  $\langle 110 \rangle$  reflections preferred to the exclusion of all others, and a small peak near the  $2\theta$  value of the  $\psi(300)$  peak appeared. After being annealed at  $500^\circ\text{C}$  for two hours (sample A) or  $510^\circ\text{C}$  for 40 minutes (sample B), the color of the film did not change. The XRD peak from  $\gamma$  decreased, that of  $\text{Au}_2\text{P}_3$  increased, and a small peak corresponding to the  $\psi(300)$  reflection was present (Fig. 2c). The SEM picture revealed that the InP substrate had been roughened, with square islands and pits about 8 microns across having formed (Fig. 1c).

#### IV. Discussion

The (111) orientation of the deposited Au film is consistent with the result of Piotrowska, et al.<sup>10</sup> who had deposited 450Å Au on (100) InP and found that it was polycrystalline with a (111) preferred orientation. However, the orientation of the Au film apparently depends upon experimental conditions. Farrow, et al.<sup>8</sup> have grown 500-5000Å thick Au films on  $\text{InP}(00\bar{1})$ , and observed the epitaxial relation  $\text{Au}(001)//\text{InP}(001)$ .

The thermodynamics of Au/InP interfacial reactions were considered by McGilp,<sup>23</sup> who calculated the enthalpy of reaction  $\Delta H_R$  for elemental Au reacting with InP to form various intermetallic compounds. McGilp concluded that the reaction of Au with InP to form the  $\alpha$  solid solution and  $\text{Au}_2\text{P}_3$  was thermodynamically feasible because  $\Delta H_R$  was negative. However, the thermochemical data used in Ref. 23 for the Au-In intermetallic compounds was actually for liquid solutions, so the resulting calculated values of  $\Delta H_R$  for various possible solid-phase reactions in the Au-In-P system must be suspect.<sup>22</sup> Furthermore, the state function that actually determines the feasibility of a reaction at constant

pressure is the Gibbs free energy. Although the change in entropy of a system is usually small for a solid state reaction, it has been shown to be important for reactions of Au with some III-V semiconductors.<sup>20</sup>

The ternary phase diagram in Fig.3 is a graphical representation of the thermodynamically stable products of all possible reactions in the Au-In-P system. It can be used to understand the sequence of the solid state reactions and the products that were observed in the thin films for the various annealing conditions. This diagram represents the solidus portion of the Au-In-P ternary phase diagram at 25°C, which is also probably valid for all temperatures up to the first eutectic point of the system. The tie-lines, which were assumed to be pseudobinary, were deduced from calculations of the enthalpy of reaction for all possible combinations of phases taken two at a time, and experimental determinations of the relative phase stability when the calculations were not definitive.<sup>22</sup> Both the  $\gamma$ -InP and  $\gamma$ -Au<sub>2</sub>P<sub>3</sub> cuts were confirmed to be pseudobinary from XRD measurements of equilibrium mixtures of appropriate amounts of Au, In, and P.<sup>22</sup>

There are 11 tie-lines in the Au-In-P system, which divide the equilateral triangle bounding the phase diagram into a set of subtriangles. These subtriangles, or tie-triangles, indicate which solid phases may coexist with one another in a bulk system at equilibrium.<sup>24</sup> An implicit assumption is that the external pressure is high enough to prevent the formation of any gas-phase species, i.e., this phase diagram is relevant as long as no P sublimes from the system. The relative amounts of Au, In, and P in a system are represented by a point that is located inside the major triangle by using the lever rule.<sup>24</sup> The phases coexisting at equilibrium are those that define the tie-triangle (or tie-line), which contains that point. For a thin film

of Au on InP, represented by an "X" on the diagram in Fig.3, the three phases bounding the tie-triangle containing the composition of the system are  $\gamma$ ,  $\text{Au}_2\text{P}_3$ , and InP. Thus, there must be a solid-state reaction between Au and InP for the system to reach equilibrium. Since there are several tie-lines between Au and InP on the phase diagram, the reaction may be expected to proceed in stages that produce intermediate reaction products, such as  $\alpha_1$ ,  $\zeta$ ,  $\zeta_1$ , and  $\epsilon$ , which form a series of intermetallic compounds with an increasing percentage of In. Each of these reactions will also produce  $\text{Au}_2\text{P}_3$ . The details of the intermediate formation will be determined by kinetic factors, such as external temperature and pressure.

If the system is closed, the overall reaction to achieve equilibrium may be represented by



and most of the reacted Au will be present in the  $\gamma$  compound. However, if the temperature is high enough to cause thermal decomposition of  $\text{Au}_2\text{P}_3$ , which has a  $P_4$  vapor pressure of about 0.6 torr at  $440^\circ\text{C}$ ,<sup>20</sup> then the composition of the system will shift to the left in Fig.3. The compounds  $\psi$ ,  $\text{AuIn}$ , or even  $\text{AuIn}_2$  may be formed, depending upon how much P sublimates from the system.

Since the Au-InP cut is not a pseudobinary tie-line, the Au/InP system is not thermodynamically stable under any circumstances and a Au film on InP may react even at room temperature.<sup>3</sup> However, the progress of a solid state reaction is limited by diffusion. Therefore, at lower temperatures, the reactions should be confined to a narrow region near the Au/InP interface, as surmised by Piotrowska, et al.<sup>10</sup>

With increasing temperature or sufficient time, the first stage of the reaction is diffusion of In and P into Au to produce  $\alpha$ , the solid solution of In in Au, and most likely  $\text{Au}_2\text{P}_3$ .

The formation of the  $\alpha$  solid solution of In in Au was detected in this work first by the formation of the spots in the Au film, as observed in the SEM micrographs of the samples annealed at room temperature. These spots were most likely the result of small regions on the film in which In had diffused up from the bulk and thus changed the work function of the surface. At this stage, the total amount of the products formed was too small to be detectable by XRD. The shoulder that developed on the Au (111) XRD peak in the samples annealed to 330°C was caused by a significant amount of  $\alpha$  ( $\sim 1/3$  of the film), but since the  $\alpha$  solution is fairly dilute, the amount of  $\text{Au}_2\text{P}_3$  that would be expected to form is still very small. The presence of  $\text{Au}_2\text{P}_3$  in our samples was not confirmed until annealing temperatures of 400°C had been reached, although  $\text{Au}_2\text{P}_3$  was observed at lower temperatures in Ref.10. A possible reason that  $\text{Au}_2\text{P}_3$  was not detected with XRD in the films annealed at the lower temperatures is that the amounts present were small and the crystallites that grew were epitaxially oriented with respect to the substrate, which would make them difficult to observe in a powder pattern.

The  $\alpha$  phase and InP do not terminate a pseudobinary tie-line, so they may react with each other to produce  $\alpha_1$  or  $\zeta$  and more  $\text{Au}_2\text{P}_3$ . Visual inspection gives a good idea of the extent of reaction of the system. At this stage, the color of the film is still yellow, because  $\alpha$ ,  $\alpha_1$ , and  $\zeta$  are all gold-colored. Higher annealing temperatures form the  $\zeta_1$  or  $\epsilon$  phases, along with more  $\text{Au}_2\text{P}_3$ . When enough  $\zeta_1$  or  $\epsilon$



has formed in the film, the color changes from yellow to pink, as occurred for annealing at 365°C.

The reactions continue until all the Au-In phases turn to  $\gamma$ , which is a silver-colored intermetallic compound. The  $\gamma$ -InP cut is a tie-line, so  $\gamma$  and InP are thermodynamically stable in a closed system. This is consistent with the fact that no further reaction was observed for annealing above 500°C in Ref.(1), and  $\gamma$  and  $\text{Au}_2\text{P}_3$  were still the major products in films annealed at 500°C and above in this study. These temperatures are above the melting point of  $\gamma$ ,<sup>18</sup> so the film beaded up and revealed substantial amounts of bare InP substrate, as shown in Fig.10.

For the highest annealing temperatures, however, a small amount of the  $\Psi$  phase was detected. This was possible because the samples were not annealed in sealed ampoules, i.e., they were open systems. At high temperatures,  $\text{Au}_2\text{P}_3$  that was formed previously in solid-state reactions can decompose via the sublimation of  $\text{P}_2$  or  $\text{P}_4$  to increase the entropy of the system.<sup>20</sup> With the loss of P, the composition of the system moves to the left in the phase diagram of Fig.3, from the  $\gamma$ - $\text{Au}_2\text{P}_3$ -InP tie-triangle into the  $\Psi$ - $\gamma$ -InP region. Thus,  $\Psi$  was observed in the films annealed at high temperatures in Ref.10 and in this work. If the temperature is high enough, or the sample is annealed under high vacuum, the  $\Psi$  phase can react with InP to release even more gas-phase phosphorus directly, as discussed in Ref.20, and both AuIn and  $\text{AuIn}_2$  can be formed, as observed in Ref.14. The chemical reactions between Au and InP were suppressed in Ref.16 by codepositing Ga. This can be understood in terms of the formation of such intermetallic compounds as AuGa and  $\text{AuGa}_2$ , which are similar enough to AuIn and  $\text{AuIn}_2$  to be essentially inert with respect to InP.

## V. Conclusions

The Au/InP interface is thermodynamically unstable at room temperature, but the interfacial reaction is kinetically limited by diffusion. In this study, as annealing temperature increased, the first step of the reaction was the interdiffusion of Au and InP to form the  $\alpha$  solid solution. Then the  $\alpha$  phase further reacted with InP to produce  $\text{Au}_2\text{P}_3$  and the pink compound  $\zeta_1$ , which in turn reacted further with InP to form more  $\text{Au}_2\text{P}_3$  and silver-colored  $\gamma$ . The phases  $\gamma$ - $\text{Au}_2\text{P}_3$ -InP define a tie-triangle in the Au-In-P phase diagram, and are thus in thermodynamic equilibrium in a closed system. In an open system, such as a vacuum chamber or under flowing  $\text{N}_2$ , other Au-In phases richer in In may be produced as a consequence of the sublimation of phosphorus, which changes the elemental composition of the system. In an open system, the most stable Au-In intermetallic contact to InP is  $\text{AuIn}_2$ , because there are no possible chemical reactions between  $\text{AuIn}_2$  and InP to form new solid phases.

## VI. Acknowledgments

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#### FIGURE CAPTIONS

- Fig.1 The SEM micrographs of Au/InP samples annealed at (a) room temperature for 35 days, (b) 365°C for 60 minutes, and (c) 510°C for 40 minutes.
- Fig.2 The X-ray diffraction pattern of a 550Å Au film on InP annealed in flowing N<sub>2</sub> at (a) 330°C for 85 min, (b) 365°C for 60min, and (c) 510°C for 40min. The peak with labeled with a \* at  $2\theta = 21.5$  is not identified; it may correspond to the (100) peak of a strained InP lattice.
- Fig.3 The solidus portion of the Au-In-P ternary phase diagram at 25°C. The topology of the diagram is valid up to the first ternary eutectic point. A dashed tie-line connects InP with  $\Psi$ , since this intermetallic compound is stable only above 224°C. However, the  $\Psi$  phase is easy to observe at room temperature by quenching.

Table I. The nine Au-In intermetallic compounds

Name	Atomic% In	Formula(s)	M.P. (°C)	$\Delta H_f$ (kcal/mole Au) <sup>a</sup>
$\alpha$	0-12.7	—	649-1064	0 ~ -2.1
$\alpha_1$	10.6-14.2	—	641-649	-1.8 ~ -2.2
$\zeta$	12.6-23.0	—	492-641	-2.1 ~ -4.2
$\zeta_1$	21.7-22.5	$\text{Au}_7\text{In}_2$	<sup>b</sup>	-4.0
$\epsilon, \epsilon'$ <sup>c</sup>	24.5-25.0	$\text{Au}_3\text{In}$	481-492	-4.0 ~ -4.3
$\gamma, \gamma'$ <sup>d</sup>	28.8-31.5	$\text{Au}_7\text{In}_3$ , or $\text{Au}_9\text{In}_4$ , or $\text{Au}_2\text{In}$	457-487	-5.2
$\psi$	35.4-39.5	$\text{Au}_3\text{In}_2$	454-458	-6.9 ~ -7.5
AuIn	50.0-50.1	AuIn	510	-10.7
$\text{AuIn}_2$	66.7	$\text{AuIn}_2$	541	-18.2

<sup>a</sup>  $\Delta H_f$  data taken directly or interpolated from values reported in Ref. 22 .

<sup>b</sup> disproportionates to  $\zeta$  and  $\epsilon$  at 337°C

<sup>c</sup> intertransformation between 299 and 339.5°C

<sup>d</sup> intertransformation between 364.5 and 374.6°C

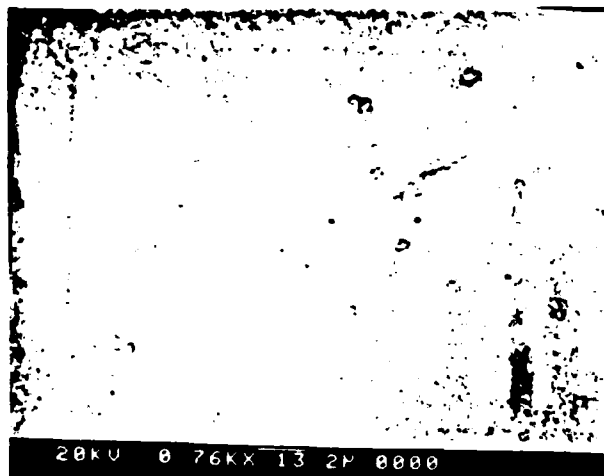
Table II. Results of annealing 550Å Au films on InP (100)

<u>Sample</u>	<u>Temperature</u>	<u>Time</u>	<u>Color</u>	<u>SEM</u>	<u>XRD</u> <sup>a</sup>
A,B	as deposited		yellow	uniform	α
A,B	25°C	35 days	yellow	spots	α
A	295°C	90 min	yellow	—	α
A	330°C	85 min	yellow	dendrites	α, ζ <sub>1</sub>
A	365°C	60 min	pink	dendrites	α, ζ <sub>1</sub> , Au <sub>2</sub> P <sub>3</sub>
A	395°C	60 min	pink	dendrites	α, ζ <sub>1</sub> , Au <sub>2</sub> P <sub>3</sub>
B	410°C	60 min	pink	—	ζ <sub>1</sub> , α, Au <sub>2</sub> P <sub>3</sub>
B	450°C	25 min	silvery	—	γ, Au <sub>2</sub> P <sub>3</sub>
		85 min	silvery	—	γ, Au <sub>2</sub> P <sub>3</sub> , ψ
A	500°C	2 hrs	silvery	—	γ, Au <sub>2</sub> P <sub>3</sub> , ψ
B	510°C	40 min	silvery	islands	γ, Au <sub>2</sub> P <sub>3</sub> , ψ

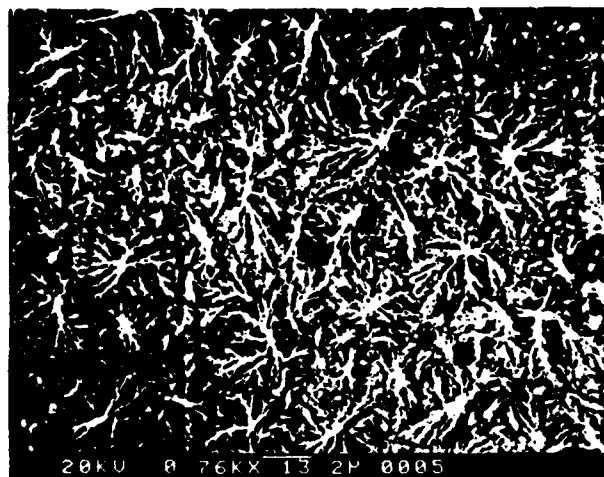
<sup>a</sup> Compounds identified in powder patterns of the films.

Fig. 1

a)



b)



c)

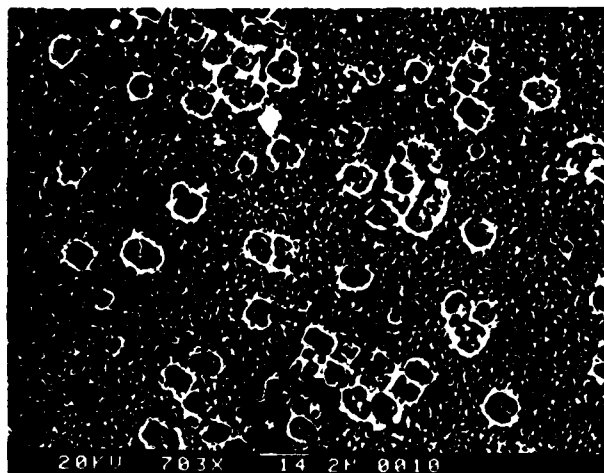




Fig. 2

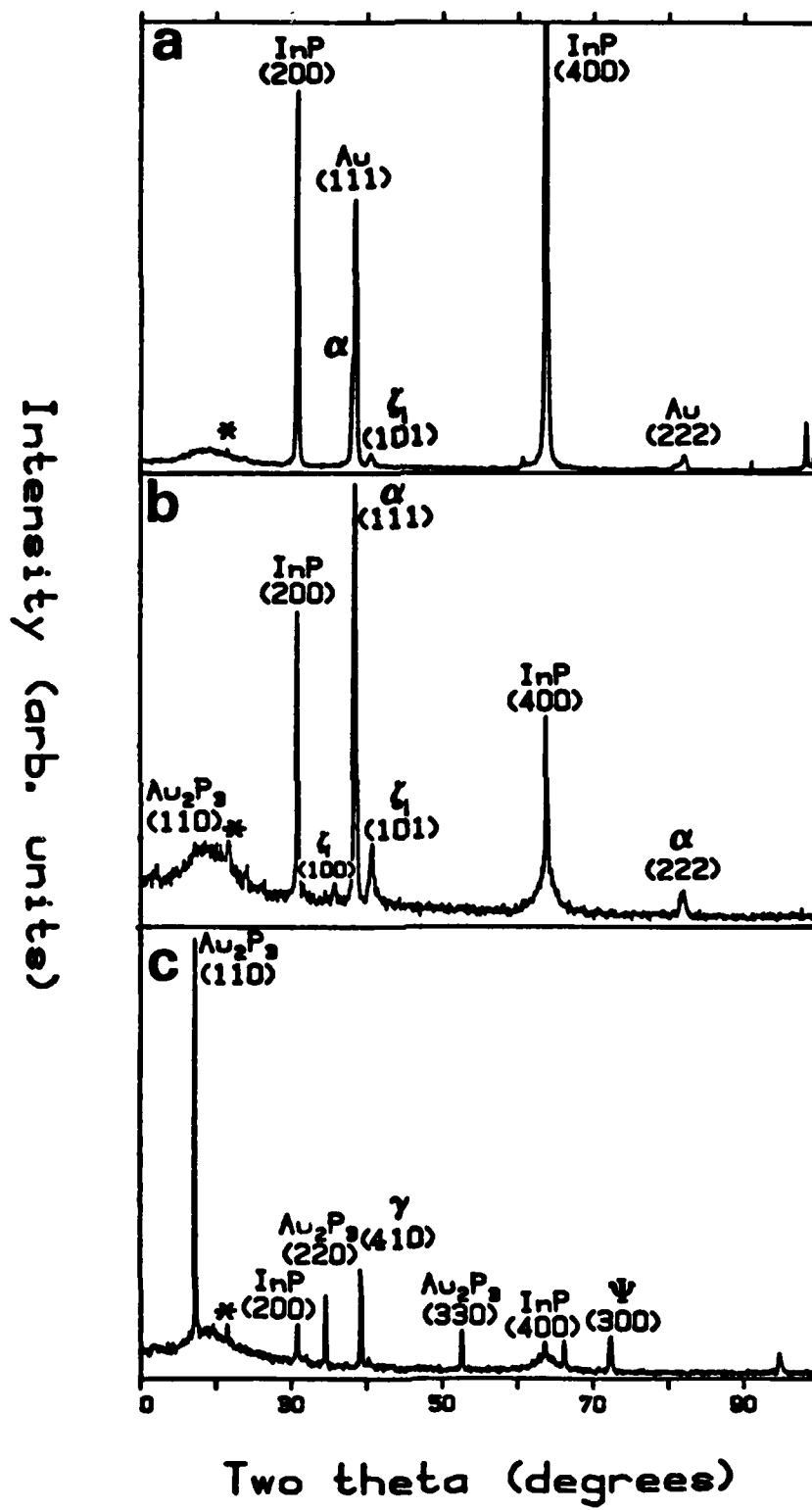
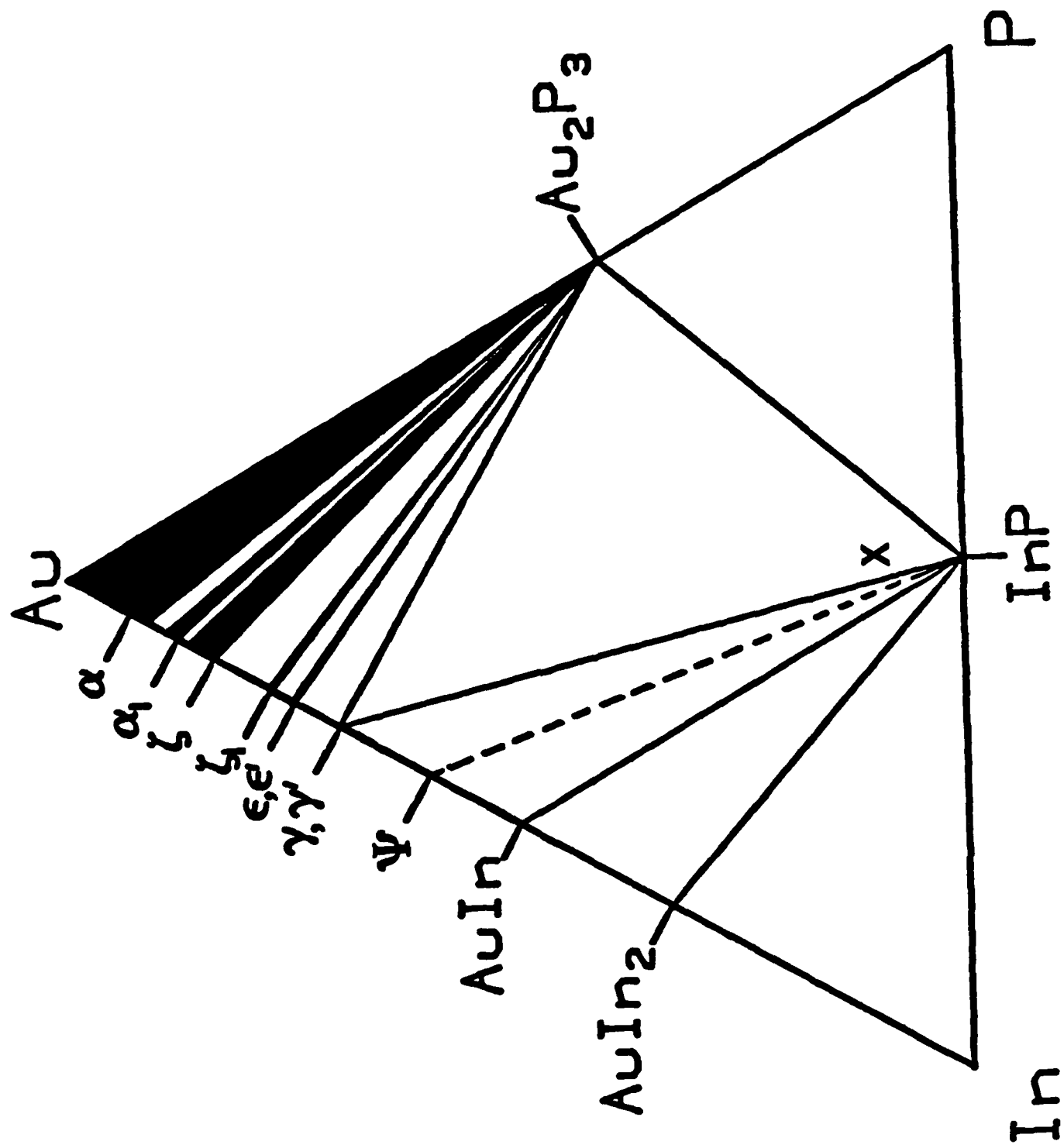


Fig. 3



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